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# Potassium based sorbents from fly ash for high temperature CO<sub>2</sub> capture

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## Abstract

Potassium-fly ash (K-FA) sorbents were investigated for high temperature CO<sub>2</sub> sorption. K-FAs were synthesised using coal fly ash as source of silica and aluminium. The synthesised materials were also mixed with Li<sub>2</sub>CO<sub>3</sub> and Ca(OH)<sub>2</sub> to evaluate their effect on CO<sub>2</sub> capture. Temperature strongly affected the performance of the K-FA sorbents, resulting in a CO<sub>2</sub> uptake of 1.45 mmol CO<sub>2</sub>/g sorbent for K-FA 1:1 at 700°C. The CO<sub>2</sub> sorption was enhanced by the presence of Li<sub>2</sub>CO<sub>3</sub> (10 wt%), with the K-FA 1:1 capturing 2.38 mmol CO<sub>2</sub>/g sorbent at 700°C in 5 min. This sorption was found to be similar to previously developed Li-Na-FA (2.54 mmol/g) and Li-FA (2.4 mmol/g) sorbents. The presence of 10% Li<sub>2</sub>CO<sub>3</sub> also accelerated sorption and desorption. The results suggest that the increased uptake of CO<sub>2</sub> and faster reaction rates in presence of K-FA can be ascribed to the formation of K-Li eutectic phase, which favours the diffusion of potassium and CO<sub>2</sub> in the material matrix. The cyclic experiments showed that the K-FA materials maintained stable CO<sub>2</sub> uptake and reaction rates over 10 cycles.

**Keywords:** Absorption, CO<sub>2</sub> sorbents, Fly ash, Potassium, CCS

## Introduction

The requirement for mitigating climate change is supporting the development of CO<sub>2</sub> capture technologies. At the state of the art, CO<sub>2</sub> absorption by liquid organic amines is the most advanced technology (Leung et al., 2014). However, amine degradation in both absorption and stripping steps and the potential emission of harmful compounds need to be addressed for a widespread commercialisation of this technology (Manzoor et al., 2014; Vega et al., 2015). The incorporation of amines into porous support has been proposed as alternative approach, but the low amine utilization ratio and the loss of amine compounds in the regeneration step required the development of new sorbents (Zhao et al., 2014).

A suitable sorbent for CO<sub>2</sub> capture from flue gas should satisfy several important criteria to compete with the present technologies, including high sorption capacity, adequate sorption/desorption kinetics and stability, mechanical strength etc. (Sabouni et al., 2014). A

large number of physical adsorbent materials have been considered for low temperature (< 150°C) CO<sub>2</sub> capture such as activated carbon, zeolites and metal organic frameworks (MOFs) (Samanta et al., 2012).

CO<sub>2</sub> capture at high temperatures (> 400°C) using solid sorbents with high selectivity and regenerability has also been proposed as an alternative to low-temperature CO<sub>2</sub> capture due to reduced efficiency penalties (Olivares-Marín et al., 2010). Due to their high decomposition temperature ( $T > 800^{\circ}\text{C}$ ), alkaline ceramics, mainly lithium containing compounds have been tested as CO<sub>2</sub> sorbents at high temperature (Rodríguez and Pfeiffer, 2008; Olivares-Marín et al., 2010). The CO<sub>2</sub> sorption on ceramics starts with the carbonation of the sorbents surface and continues with the diffusion of CO<sub>2</sub> through the carbonate external layer to react with the alkaline core (Rodríguez and Pfeiffer, 2008). So far, potassium has been mainly investigated as CO<sub>2</sub> sorption promoter associated to other ceramics such as Li- or Na- based sorbents, zeolites and alumina based CO<sub>2</sub> sorbents (Seggiani et al., 2013; Zhao et al., 2014; Olivares-Marín et al., 2010; Sanna et al., 2014; Sanna et al., 2015).

Amongst the wide range of materials tested, lithium silicate (Li<sub>4</sub>SiO<sub>4</sub>) and aluminate (Li<sub>5</sub>AlO<sub>4</sub>) have shown the largest CO<sub>2</sub> sorption capacity and the fastest CO<sub>2</sub> sorption rate over a wide range of temperatures and CO<sub>2</sub> concentrations (Olivares-Marín et al., 2010; Kato et al., 2005, Flores-Martínez and Pfeiffer, 2015). It has been reported that the presence of 40 mol% K<sub>2</sub>CO<sub>3</sub> at 600°C affects the CO<sub>2</sub> sorption capacity for Li-based sorbents (Li-FA) prepared from fly ashes (FA), with a sorption capacity of 2.43 mmol CO<sub>2</sub>/g sorbent (Olivares-Marín et al., 2010). Recently, sodium-fly ash (Na-FA) sorbents have also been proposed as high temperature CO<sub>2</sub> sorbents. Maximum CO<sub>2</sub> uptake of Na-FA sorbent was found to be 2 mmol CO<sub>2</sub>/g sorbent in presence of 20% Li<sub>2</sub>CO<sub>3</sub> additive (Sanna et al., 2014; Sanna et al., 2015). Even if lithium based materials present very good CO<sub>2</sub> uptake performance, it should be noted that lithium is considered a rare element in comparison to sodium and potassium. It has been assessed that demand for lithium is growing at a fast rate and that this rate exceeds projected availability by 25% (The Financialist, 2014). Therefore, K-based sorbents can be considered not rare compared to lithium based materials.

The use of potassium carbonate, in addition to other alkali-metal materials was firstly studied by NASA for space applications (Onischak et al, 1978). Also, potassium has been previously identified as a good candidate for low temperature CO<sub>2</sub> sorption while utilizing an activated carbon as support (Hayashi et al., 1998). In addition, silver carbonate in combination with

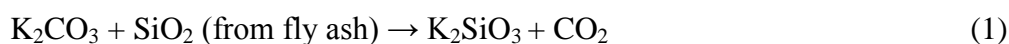
alkali metal silicate (including potassium), alkali metal carbonate (potassium and/or sodium) have been evaluated as CO<sub>2</sub> sorbent (Nalette et al., 1992).

Thermodynamic analysis including enthalpy and free energy changes have been calculated for both K-silicate sorption and regeneration reactions (Hoffman and Pennline, 2001). Results for alkali-based sorbents are generally favourable in that the forward (CO<sub>2</sub> absorption) reaction rate is typically much larger than the reverse reaction. Potassium carbonate was found to be suitable for CO<sub>2</sub> capture at low absorption temperatures (less than 145°C), while calcium oxide is more suitable for high absorption temperatures (less than 860°C) (Hoffman and Pennline, 2001). For this reason, potassium-based sorbents have been proposed as effective ambient temperature CO<sub>2</sub> sorbent in confined spaces (Zhao et al., 2014). The CO<sub>2</sub> sorption capacities were calculated as 0.87, 1.18, 0.34, 0.53, and 0.15 mmol CO<sub>2</sub>/g for K<sub>2</sub>CO<sub>3</sub>/Activate carbon, K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>/zeolite-5A and K<sub>2</sub>CO<sub>3</sub>/13X-zeolite, respectively.

Despite the fact that potassium carbonate has been widely tested as CO<sub>2</sub> capture promoter (Olivares-Marín et al., 2010; Seggiani et al, 2011; Flores-Martínez and Pfeiffer, 2015; Sanna et al, 2015), there is a lack of works on the potential use of K-silicates derived from fly ash as high temperature CO<sub>2</sub> sorbents and their behaviour when used in presence of CO<sub>2</sub> sorption promoters. Moreover, previous studies have only examined the CO<sub>2</sub> capture behaviours of alkali metal-based sorbents under conditions of 50–100°C, 5–20% CO<sub>2</sub> and 5–20% H<sub>2</sub>O (Zhao et al, 2011; Zhao et al, 2013; Zhao et al, 2014). It is unclear whether CO<sub>2</sub> sorption capacity changes at higher temperatures. The aim of the present work was to produce pure and Li-doped aluminosilicates from fly ash and assess their CO<sub>2</sub> sorption capacity under different conditions.

## Experimental

Fly ashes (FA) have been used as SiO<sub>2</sub> source and collected from a cyclone filter. The parent sample was characterised by particles size distribution and XRF in previous work (A. Sanna et al, 2015). The potassium based CO<sub>2</sub> sorbents were synthesised by mixing the FA with K<sub>2</sub>CO<sub>3</sub> (Acros Organics) at different K<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub> (from FA) molar ratios (2:1 and 1:1) by using an agate mortar and pestle. The mixed powders were calcined in a muffle furnace at 800°C for 8 hours. The sorbent synthesis is described as follow:



After calcination, the materials were homogenised using a Mortar Grinder (Pulverisette 2, Fritsch) for 60 seconds to eliminate any potential agglomeration.  $\text{Ca}(\text{OH})_2$  and  $\text{Li}_2\text{CO}_3$  were also used as  $\text{CO}_2$  sorption promoters (10 mol%) by addition after the calcination step.

The resulting sorbents were grinded and characterized by different techniques, including powder X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) and Fourier Transformed Infrared (FTIR). A Bruker Nonius X8-Apex2 CCD diffractometer equipped with an Oxford Cryosystems Cryostream, typically operating at 100 K was used for the XRD analysis. A PerkinElmer Frontier infrared spectrometer was used to gain additional information on the crystal structure of the synthesised sorbents before and after the  $\text{CO}_2$  absorption experiments.

The  $\text{CO}_2$  capture capacity of the resultant samples was measured by using a TGA (TA Q500). About 15 mg of sample was loaded in the TGA pan for each experiment. Prior to  $\text{CO}_2$  sorption testing, the samples were dried in  $\text{N}_2$  flow (95 mL/min) for 1 hr at the same temperature used for the  $\text{CO}_2$  sorption (600, 700 °C). The heating rate used to rise the temperature to 600 or 700°C (before holding it for 1hr) was 25 °C/min. Then, the  $\text{CO}_2$  absorption tests were performed by flowing 100%  $\text{CO}_2$  gas at the desired temperature. The weight increase due to  $\text{CO}_2$  sorption (mmol  $\text{CO}_2$ /g sorbent) was measured as a function of time at a constant temperature (600, 700 °C) and constant concentration of  $\text{CO}_2$  or flue gas (95 mL/min) at atmospheric pressure.  $\text{CO}_2$  uptake was calculated based on dry sorbents weight (after drying step). Triplicate measurements were conducted to estimate the % error in the experimental work. The measurements error (calculated as the standard deviation of triplicates) resulted lower than 5%. The  $\text{CO}_2$  desorption step was carried out at the same sorption temperature by switching the furnace atmosphere from  $\text{CO}_2$  to  $\text{N}_2$  for 1hr. Finally, ten (five for the sorbent with 10%  $\text{Li}_2\text{CO}_3$  additive) regeneration cycles were used to ascertain the stability for selected sorbents.

## Results & Discussion

### Sorbents characterisation

The  $\text{CO}_2$  capture reaction in presence of potassium silicate is described by the equation:



The reaction thermodynamics (Table 1) indicate that the capture reaction is overall spontaneous ( $\Delta G < 0$ ), and at temperatures  $< 100^\circ\text{C}$   $\Delta S$  and  $\Delta H$  are negative, indicating exothermic reaction. However, similarly to other alkali silicates, this experimental work clearly indicates that  $\text{CO}_2$  capture is favoured at high temperature (Sanna et al., 2014).

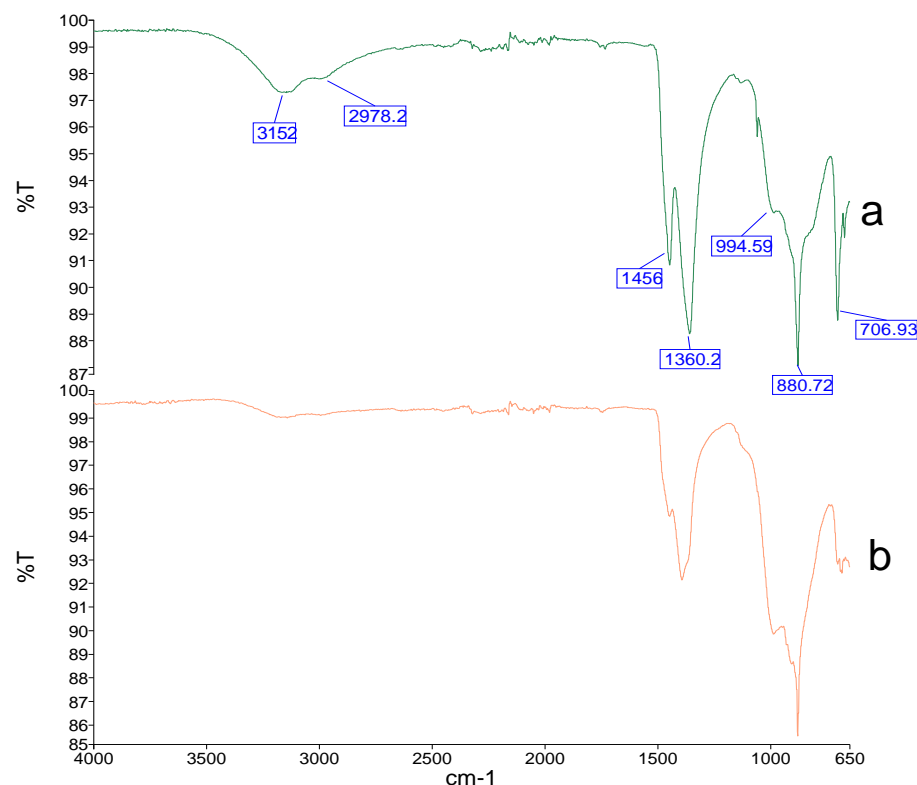
**Table 1.** Thermodynamics of  $\text{CO}_2$  capture by K-FA in gas phase at different temperatures.

| T, $^\circ\text{C}$ | deltaH, kJ | deltaS, J/ $^\circ\text{K}$ | deltaG, kJ | K       | Log(K) |
|---------------------|------------|-----------------------------|------------|---------|--------|
| 0                   | -1409.8    | -165.2                      | -1364.7    | 1.E+261 | 261.0  |
| 100                 | -1397.1    | -125.7                      | -1350.2    | 1.E+189 | 189.0  |
| 200                 | -1382.4    | -90.9                       | -1339.4    | 8.E+147 | 147.9  |
| 300                 | -1365.9    | -59.4                       | -1331.9    | 2.E+121 | 121.4  |
| 400                 | -1347.6    | -30.0                       | -1327.4    | 1.E+103 | 103.0  |
| 500                 | -1327.3    | -1.7                        | -1326.0    | 4.E+89  | 89.6   |
| 600                 | -1307.9    | 21.9                        | -1327.0    | 2.E+79  | 79.4   |
| 700                 | -1289.2    | 42.2                        | -1330.2    | 3.E+71  | 71.4   |
| 800                 | -1269.8    | 61.1                        | -1335.4    | 1.E+65  | 65.0   |
| 900                 | -1220.1    | 104.5                       | -1342.6    | 6.E+59  | 59.8   |
| 1000                | -1198.0    | 122.5                       | -1353.9    | 4.E+55  | 55.6   |

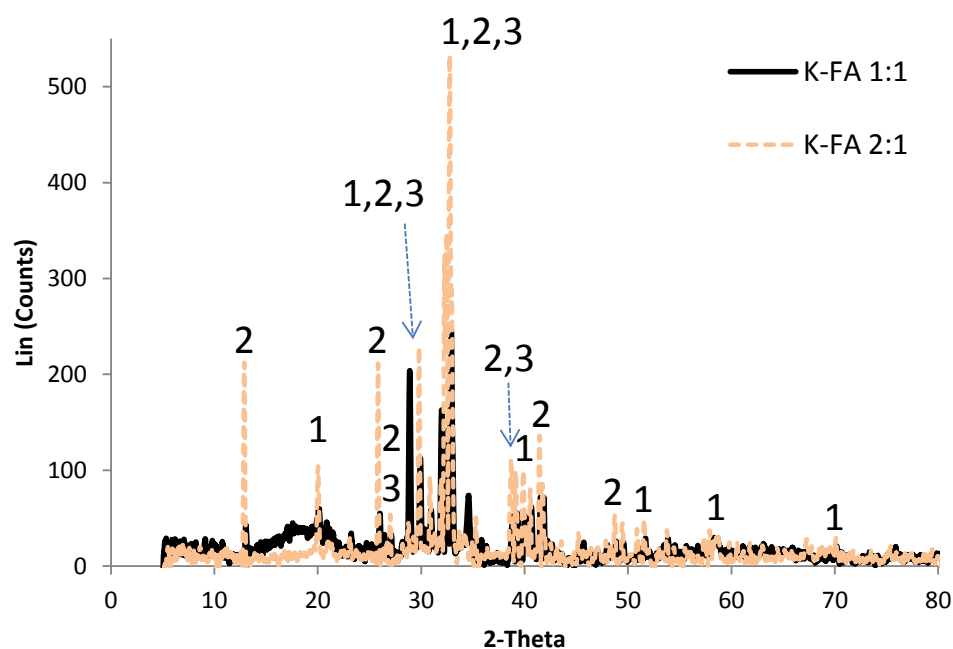
The major chemical bonds present in the synthesised alkali metals silicate were identified by FTIR spectra, as shown in Fig. 1. The characteristic absorption band from deformation of  $\text{M}^+\text{OH}$  become  $\text{Si-O-M}^+$  are shown at  $880$  and  $994\text{ cm}^{-1}$  (Hindryawati et al, 2014), while the predominant absorbance peak at  $1360\text{ cm}^{-1}$  is due to siloxane bonds ( $\text{Si-O-Si}$ ) (Thuadaj et al, 2008). The peak at  $1427\text{ cm}^{-1}$  can be attributed to  $\text{CO}_3^{2-}$  anion originating from the potassium carbonate. As reported in previous work, the broadband between  $2800$  and  $3500\text{ cm}^{-1}$  is attributed to silanol OH groups and adsorbed water (Kalapathy et al, 2000). The FTIR spectra show formation of silicate structure.

Figure 2 shows the XRD patterns of the synthesised K-FA. It was found that the X-ray diffraction patterns of the two materials contain identical peaks but with different intensities. The major peaks were identified and compared to potassium metasilicate ( $\text{K}_2\text{SiO}_3$ ), potassium aluminium silicate ( $\text{K}_{1.25}\text{Al}_{1.25}\text{Si}_{0.75}\text{O}_4$ ) and potassium carbonate ( $\text{K}_2\text{CO}_3$ ) using XRD database and previous publication (N. Hindryawati et al, 2014). It was found that K-FA 1:1 structure presented a less defined crystal structure (see theta region between  $15$  and  $25$ ) and with the increase of  $\text{K}_2\text{CO}_3$  used in the  $\text{K}_2\text{CO}_3$ :FA mixture (2:1), the materials structure become more crystalline. The intense diffraction sharp peaks from  $12$  to  $43$  are associated to potassium metasilicate and potassium aluminium metasilicate, while the sharp diffraction peaks at  $12$  and  $26$  are solely attributed to  $\text{K}_2\text{SiO}_3$ . As can be seen in Figure 1, K-FA 2:1

presents more intense peaks ( $1456\text{ cm}^{-1}$ ) related to  $\text{K}_2\text{CO}_3$ . This indicates a not complete reaction during synthesis, probably due to poor contacts between  $\text{K}_2\text{CO}_3$  and  $\text{SiO}_2$  from FA.



**Figure 1.** FTIR of (a) K-FA 2:1 (b) K-FA 1:1.



**Figure 2.** XRD patterns of K-FA 1:1 and K-FA 2:1. Mineral phases identified: 1 Potassium aluminium silicate; 2 Potassium carbonate; 3 Potassium metasilicate.

## CO<sub>2</sub> capture studies

CO<sub>2</sub> capture experiments were carried out using the synthesized K-sorbents shown in Table 2. The K-FA sorbents capacity was compared to those of Li-based and Li/Na-based fly ash sorbents previously developed by our group (Olivares-Marin et al, 2010; Sanna et al, 2015). The sorption experiment at 500°C was used to compare the K-FA sorbent prepared here to the Li-FA sorbent, while the sorption at 600°C was used to evaluate the differences with the Li-Na-FA sorbents. Table 2 shows that the K-FA 1:1 CO<sub>2</sub> sorption capacity was three times higher than that of Li-FA under the same conditions, while K-FA 2:1 possesses a CO<sub>2</sub> sorption capacity double than that of Li-FA. The K-FA materials had however a lower capacity compared to the Li-Na-FA sorbent at both 500 and 600°C.

Table 2 also shows a clear difference in the CO<sub>2</sub> sorption capacity when different K<sub>2</sub>CO<sub>3</sub>:FA molar ratio were used. The K-FA sorbent shows better performance at molar ratios 1:1 (0.32, 0.36 and 1.45 mmol CO<sub>2</sub> / g sorbent at 500, 600 and 700°C, respectively), while a K-FA ratio of 2:1 was able to chemisorb only 0.23, 0.36, 0.82 mmol CO<sub>2</sub> / g sorbent at the same temperatures. This can be related to the different distribution of mineral phases formed during the sorbent synthesis (see Figure 2), and a large presence of unreacted K<sub>2</sub>CO<sub>3</sub> is present in the K-FA 2:1 (see Figure 1).

**Table 2.** Summary of the CO<sub>2</sub> capture experiments in presence of 100%CO<sub>2</sub>. 1:1 represents the K<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub> (FA) molar ratio.

|   |           |                                    | CO <sub>2</sub> sorption capacity |      |
|---|-----------|------------------------------------|-----------------------------------|------|
|   |           |                                    | mmol CO <sub>2</sub> / g sorbent  |      |
| Sample  | Temp., °C | Additive (mol%)                    | 1 h                               | 2h   |
| Olivares-Marín et al., 2010   |           |                                    |                                   |      |
| FA-Li <sub>4</sub> SiO <sub>4</sub> (1 SiO <sub>2</sub> : 2 Li <sub>2</sub> CO <sub>3</sub> ) | 500       |                                    | < 0.11                            | na   |
| FA-Li <sub>4</sub> SiO <sub>4</sub> (1 : 2)   | 600       | 10% K <sub>2</sub> CO <sub>3</sub> | 0.59                              | na   |
| FA-Li <sub>4</sub> SiO <sub>4</sub> (1 : 2)   | 600       | 20% K <sub>2</sub> CO <sub>3</sub> | 1.27                              | na   |
| FA-Li <sub>4</sub> SiO <sub>4</sub> (1 : 2)   | 650       | 10% K <sub>2</sub> CO <sub>3</sub> | 0.48                              | na   |
| Sanna et al., 2015  |           |                                    |                                   |      |
| Li/Na-FA (0.5:0.5:1)  | 500       |                                    | 0.48                              |      |
| Li/Na-FA (1:1:1)  | 600       |                                    | 0.86                              | 1    |
| This work   |           |                                    |                                   |      |
| K-FA 1:1  | 500       |                                    | 0.32                              | 0.34 |
| K-FA 1:1  | 600       |                                    | 0.36                              | 0.39 |
| K-FA 2:1  | 500       |                                    | 0.23                              | 0.27 |
| K-FA 2:1  | 600       |                                    | 0.36                              | 0.45 |
| K-FA 2:1  | 700       |                                    | 0.82                              | 0.86 |
| K-FA 1:1  | 700       |                                    | 1.45                              | 1.50 |



## Effect of temperature and CO<sub>2</sub> promoters

Figures 3 and 4 show the effect of temperature on the CO<sub>2</sub> capacity. The initial weight decrease was obtained in presence of N<sub>2</sub> flow, and represents desorption of absorbed water. The CO<sub>2</sub> sorption experiments indicate that K-FA 1:1 and 2:1 increase their CO<sub>2</sub> sorption capacity with temperature, with maximum sorption taking place at 700°C. This trend did not differ from that previously found in presence of Li- and Li-Na- silicate sorbents (Sanna et al, 2015). As shown in Table 2, the K-Fa 2:1 CO<sub>2</sub> uptake (0.82 mmol CO<sub>2</sub>/g sorbent after 1 hour at 700°C) is about half compared to the CO<sub>2</sub> absorbed by using K-FA 1:1 at the same temperature (1.45 mmol CO<sub>2</sub>/g sorbent). Not only the CO<sub>2</sub> sorption capacity was higher at 700°C, but also the sorption rate was faster as indicated by the slope of the sorption profiles in Figures 3 and 4. However, full desorption was not achieved under the studied conditions, as CO<sub>2</sub> desorption did not occur with both K-FA 1:1 and 2:1 and even in presence of K-FA doped with Ca(OH)<sub>2</sub>. Also, sorption took longer to achieve maximum capacity compared to using Li-FA sorbents under the same conditions, which results too long for industrial applications (Sanna et al, 2015; Olivares-Marín et al, 2010).

Since the pure K-FA silicates failed to desorb the CO<sub>2</sub>, a series of experiments were carried out to establish if the desorption could be improved by the presence of additives. Since previous works indicated that Li<sup>+</sup> provides the highest CO<sub>2</sub> capture capacity among all the univalent cations, if provided in the same amount in the ceramic (Walton et al, 2006; Ridha et al, 2009), was selected Li<sub>2</sub>CO<sub>3</sub> as sorbent promoter and Na<sub>2</sub>CO<sub>3</sub> and Ca(OH)<sub>2</sub> for comparison.

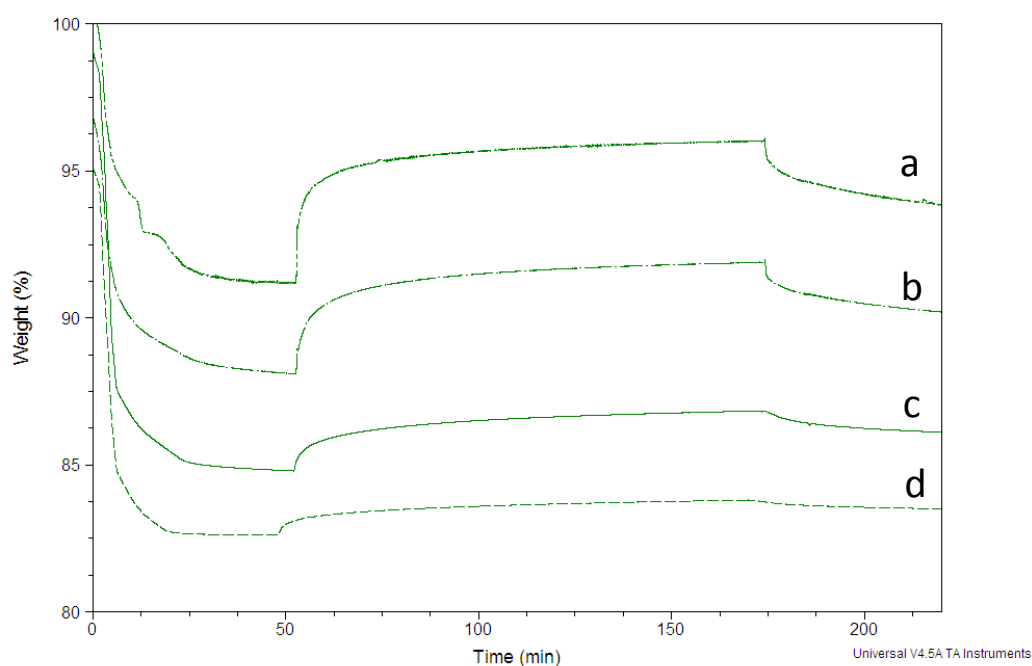
Figure 3 compares the CO<sub>2</sub> working capacity of K-FA 2:1 with and without Ca(OH)<sub>2</sub> at 700°C. The pure K-FA 2:1 sample captured 0.82 mmol CO<sub>2</sub>/g. The CO<sub>2</sub> captured increased to 1.04 mmol/g in presence of 10% Ca(OH)<sub>2</sub>. Despite this, the Ca-additive was not able to promote CO<sub>2</sub> desorption, indicating the formation of a products layer (carbonates and oxides), which prevents CO<sub>2</sub> desorption. The addition of 10% Li<sub>2</sub>CO<sub>3</sub> to K-FA 2:1, further increased the CO<sub>2</sub> sorption to 2.25 mmol CO<sub>2</sub>/g as can be seen in Figure 6-a. Therefore, the presence of Li<sub>2</sub>CO<sub>3</sub> promoted the CO<sub>2</sub> uptake and also the CO<sub>2</sub> sorption rate, as can be seen comparing the slopes in the sorption profiles in Figures 3 and 6-a.

Different additives were tested in the weight ratio of 10% using the K-FA 1:1 sorbent at 700°C, as presented in Figure 5. Figure 5-c indicates that the initial desorption of absorbed water in N<sub>2</sub> required longer time, so that the real CO<sub>2</sub> working capacity is larger than shown in Figure 6-b. Both Na<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> were successful in desorbing all the CO<sub>2</sub> previously

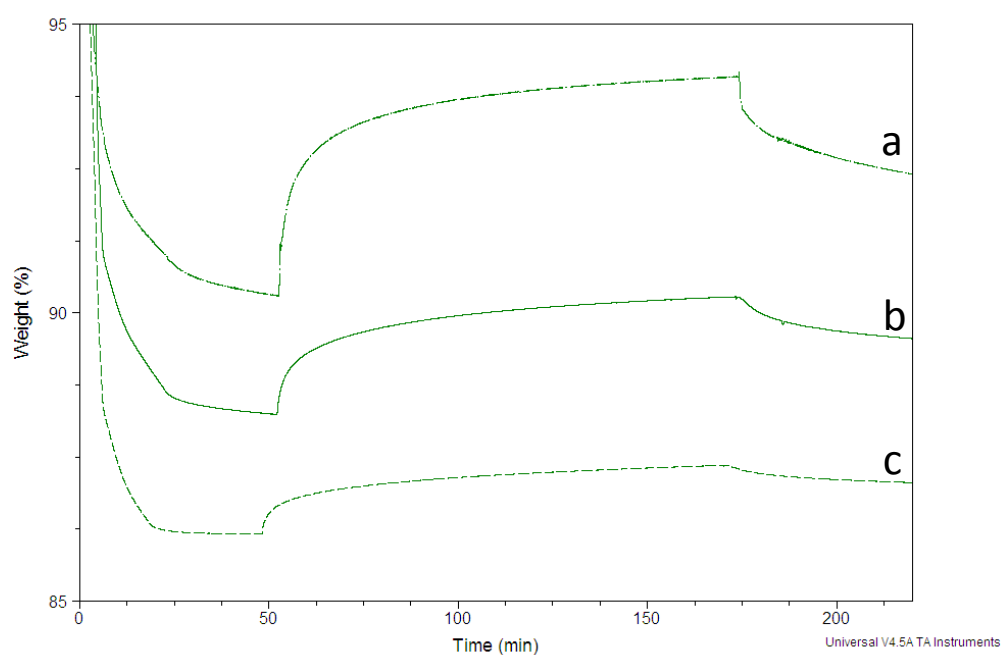
absorbed. The CO<sub>2</sub> loading capacity was also enhanced to 2.39 mmol CO<sub>2</sub>/g sorbent from 1.45 mmol/g in presence of Li<sub>2</sub>CO<sub>3</sub>. Moreover, fast sorption and desorption in presence of 10% Li<sub>2</sub>CO<sub>3</sub> were achieved, requiring only minutes to fully uptake the CO<sub>2</sub> and about 20 minutes to desorbing it. The synergic effect of adding 10% Li<sub>2</sub>CO<sub>3</sub> can be explained with full activation of the Li-K eutectic melt at around 700°C, which increased CO<sub>2</sub> capacity and sorption rate (Sanna et al, 2015; Flores-Martínez and Pfeiffer, 2015). The CO<sub>2</sub> sorption capacities in presence of K-FA 1:1 and 2:1 were comparable to those shown by Li-FA sorbents (0.48 mmol CO<sub>2</sub>/g sorbent) in presence of 10% K<sub>2</sub>CO<sub>3</sub> additive at 650°C (Olivares-Marín et al, 2010). In the same study, 40% K<sub>2</sub>CO<sub>3</sub> was required (at 600°C) to absorb 2.43 mmol CO<sub>2</sub>/g sorbent.

Based on our observations and previous works (Ortiz-Landeros et al, 2012; Sanna et al, 2015; Flores-Martínez and Pfeiffer, 2015), the different CO<sub>2</sub> sorption capacities and rates observed at 500, 600 and 700°C can be explained by surface chemisorption limited by the formation of external shell containing an KAlO<sub>2</sub> secondary phase and Li<sub>2</sub>CO<sub>3</sub> product at temperatures up to 500°C. Between 500 and 600°C, partial molten generated by eutectic phases starts to promote diffusion processes and then, at about 700°C, the CO<sub>2</sub> chemisorption is kinetically controlled by diffusion processes (Flores-Martínez and Pfeiffer, 2015; Sanna et al, 2015).

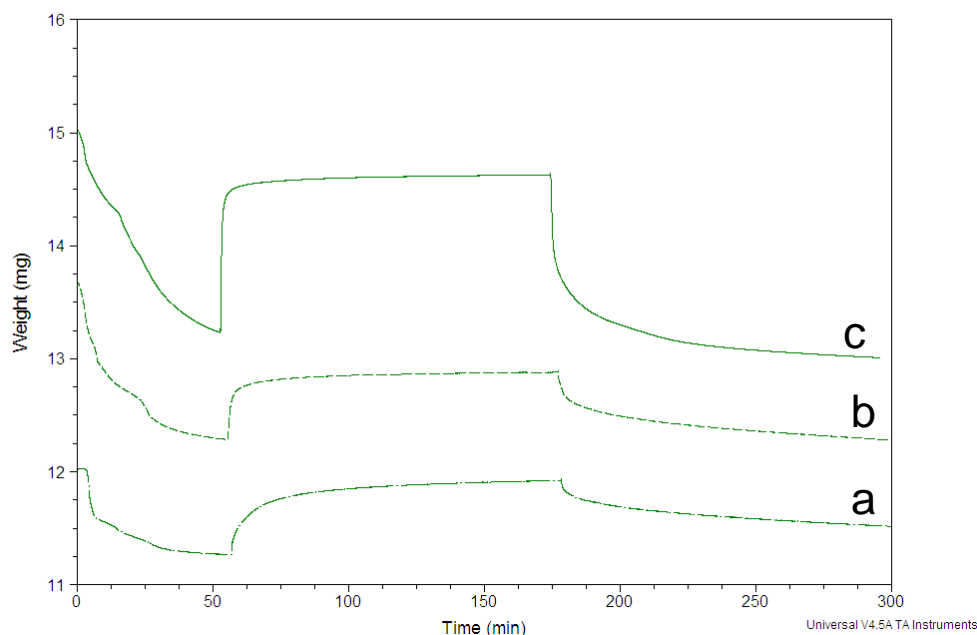
Moreover, it has been indicated that the binary compound K<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub> (KAlO<sub>2</sub>) shows that at ambient pressure, KAlO<sub>2</sub> consists of tetragonal crystals between 1350 and 600°C (γ-KAlO<sub>2</sub>) and orthorhombic crystals below 600°C (β-KAlO<sub>2</sub>), with the structural re-arrangement comparable with that of NaAlO<sub>2</sub> and LiAlO<sub>2</sub> (de Kroon et al, 2001). Even if isolated silicates present melting points well above 700°C, compounds with the composition Na<sub>1.55</sub>K<sub>0.45</sub>Si<sub>2</sub>O<sub>5</sub> have eutectic decomposition temperature at 696°C (Yazhenskikh et al, 2008). The Li cations can decrease the melting point of the sorbent enhancing the diffusion of the species on the sorbent surface, which results in enhanced CO<sub>2</sub> sorption capacity and CO<sub>2</sub> sorption/desorption rates. Moreover, the formed eutectic phases in presence of Li<sub>2</sub>CO<sub>3</sub> clearly increase the carbonate decomposition processes by enhancing the diffusion of cations and CO<sub>2</sub>, enabling the recyclability of the material, as shown in Figure 5 (Flores-Martínez and Pfeiffer, 2015).



**Figure 3.** TGA of (a) K-FA 2:1 700°C+10%  $\text{Ca(OH)}_2$ ; (b) K-FA 2:1 700°C; (c) K-FA 2:1 600°C; (d) K-FA 2:1 500°C.



**Figure 4.** TGA of (a) K-FA 1:1 700°C; (b) K-FA 1:1 600°C; (c) K-FA 1:1 500°C.



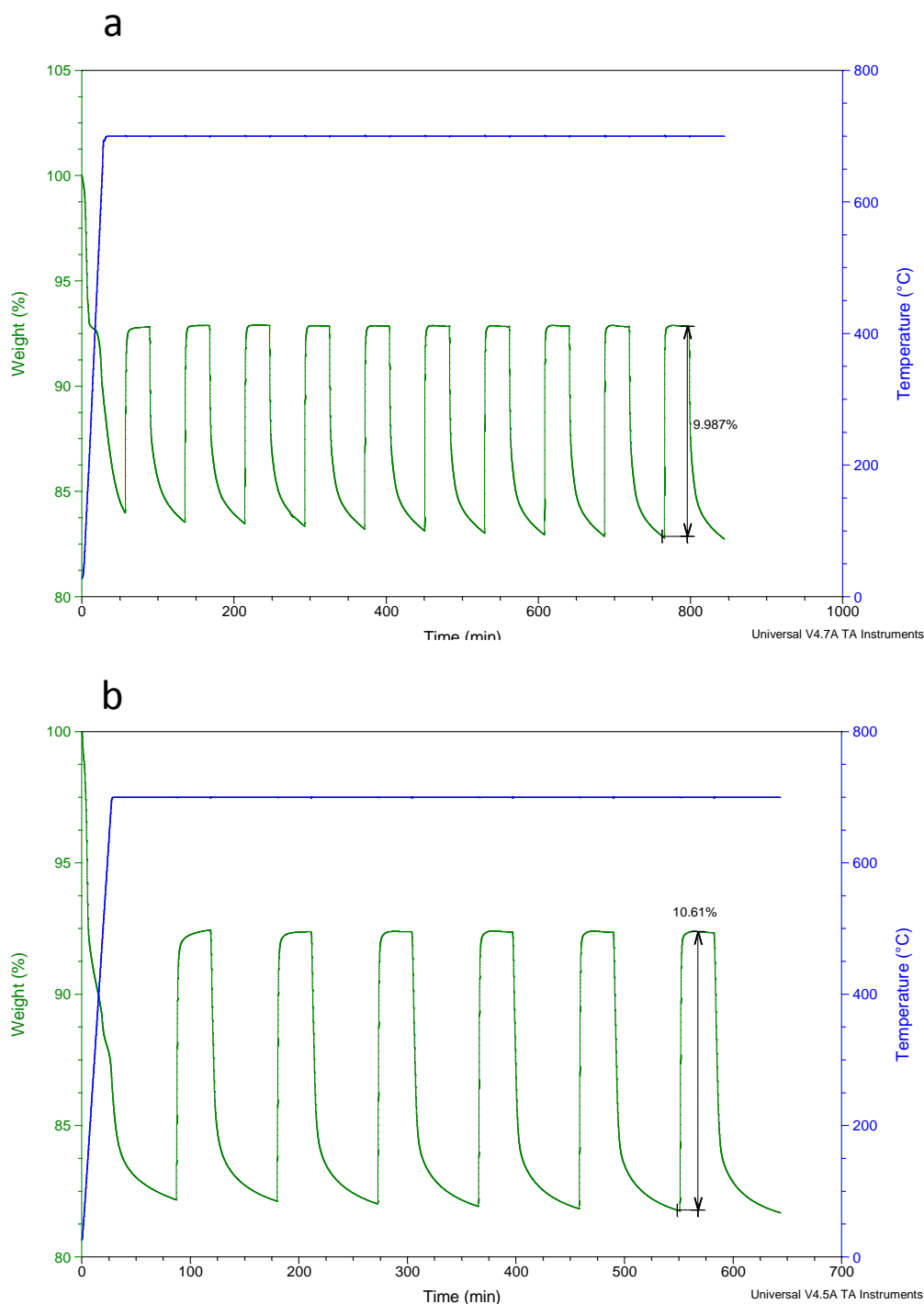
**Figure 5.** TGA of (a) K-FA 1:1; (b) K-FA 1:1+10%  $\text{Na}_2\text{CO}_3$ ; (c) K-FA 1:1+10%  $\text{Li}_2\text{CO}_3$ .

### Sorbents regeneration

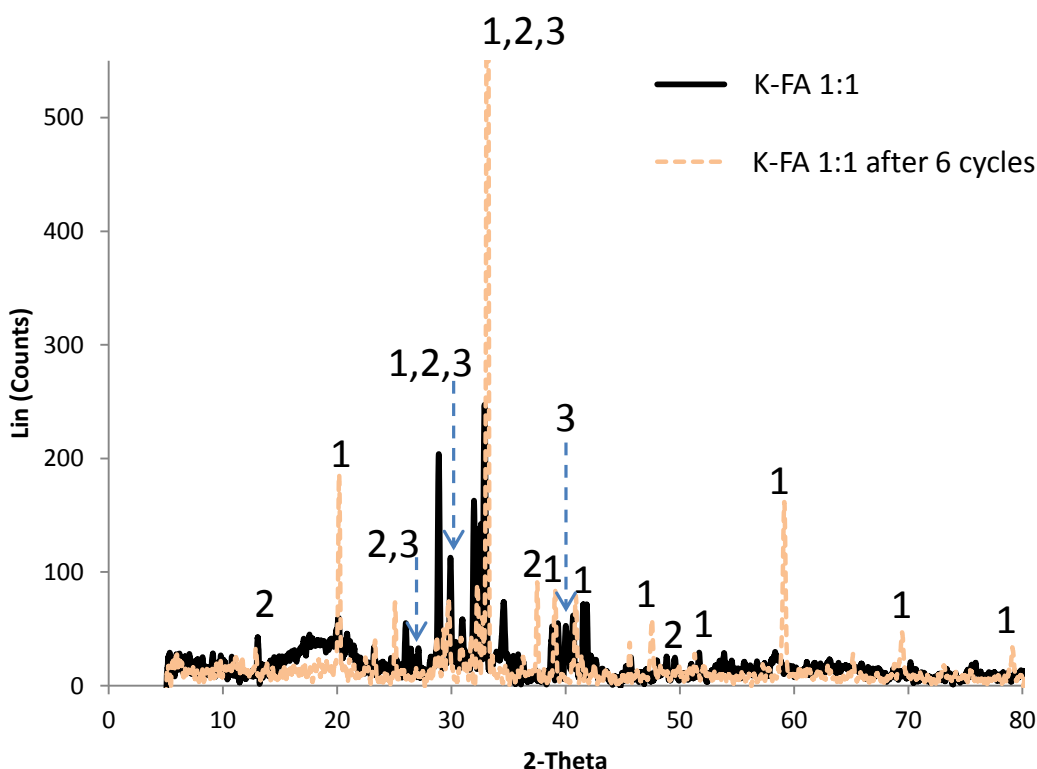
Figure 6 shows 10 and 6  $\text{CO}_2$  sorption/desorption cycles for the Na-FA sorbent with  $\text{K}_2\text{CO}_3:\text{SiO}_2$  molar ratios of 2:1 and 1:1 in presence of 10%  $\text{Li}_2\text{CO}_3$ . Both K-FA 2:1 and 1:1 were able to maintain 100%  $\text{CO}_2$  sorption capacity at  $700^\circ\text{C}$ , respectively after 10 and 6 cycles. K-FA 1:1 showed a slightly increase of the  $\text{CO}_2$  sorption cycle after cycle, which could be ascribed to the not completed initial desorption under  $\text{N}_2$  atmosphere before the cyclic  $\text{CO}_2$  sorption/desorption. K-FA presented superior cyclic stability compared to other high temperature absorbents, such as hydrotalcites, where the capacity of the latter decrease after a number of cycles (Maroño et al, 2014).

K-Fa 1:1 with 10%  $\text{Li}_2\text{CO}_3$  after 6 sorption/desorption cycles was analyzed by XRD to establish any structural change in relation to the increased  $\text{CO}_2$  uptake capacity shown after 6 cycles. The XRD patterns of the starting K-FA 1:1 and the K-FA after 6 cycles are shown in Figure 7, which indicates that, the sorption/desorption cycles affects the mineral composition of these materials. In fact, there was an increase of sodium aluminium silicate phase and a decrease of the abundance of metasilicate phases. This behavior was already observed in our previous work using Li-Na-FA silicates (Sanna et al, 2015). Both TGA and XRD data suggest that the crystals structure modification improves the  $\text{CO}_2$  sorption, which may be

284 related to enhanced K species diffusion due phase change (from solid to liquid-like) of  
 285 eutectic Na-meta-silicates phases in presence of impurities such as K, Ca and Mg oxides  
 286 (from fly ash) as indicated in previous work (Sanna et al, 2015; Flores-Martínez and Pfeiffer,  
 287 2015).



288 **Figure 6.** Cyclic stability at 700°C of a) K-FA 2:1 and b) K-FA 1:1 under 100%CO<sub>2</sub> atmosphere and in  
 289 presence of 10% Li<sub>2</sub>CO<sub>3</sub>. Temperature profile shown in y2-axes.  
 290



**Figure 7.** XRD pattern of raw K-FA and K-FA after 6 absorption/desorption cycles. 1 Potassium aluminium silicate ( $K_{1.25}Al_{1.25}Si_{0.75}O_4$ ); 2 Potassium carbonate; 3 Potassium metasilicate.

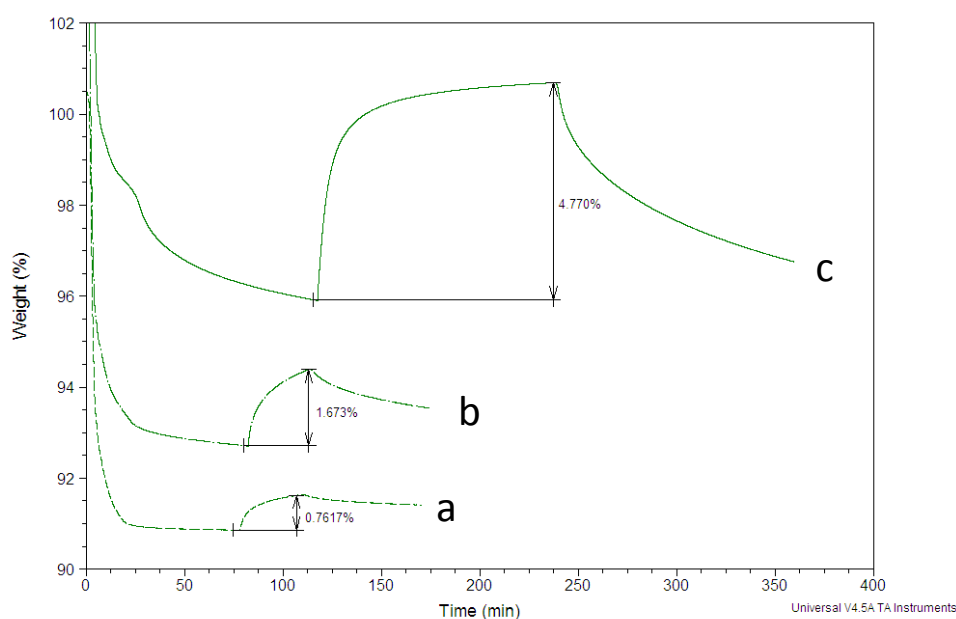
### Presence of diluted $CO_2$ and potential scale up

The use of solid sorbents for  $CO_2$  capture implies that the selected materials present rapid  $CO_2$  sorption/desorption rates and high  $CO_2$  sorption capacity. This is required due to the diluted  $CO_2$  in flue gas, which results in large volumes to be treated.

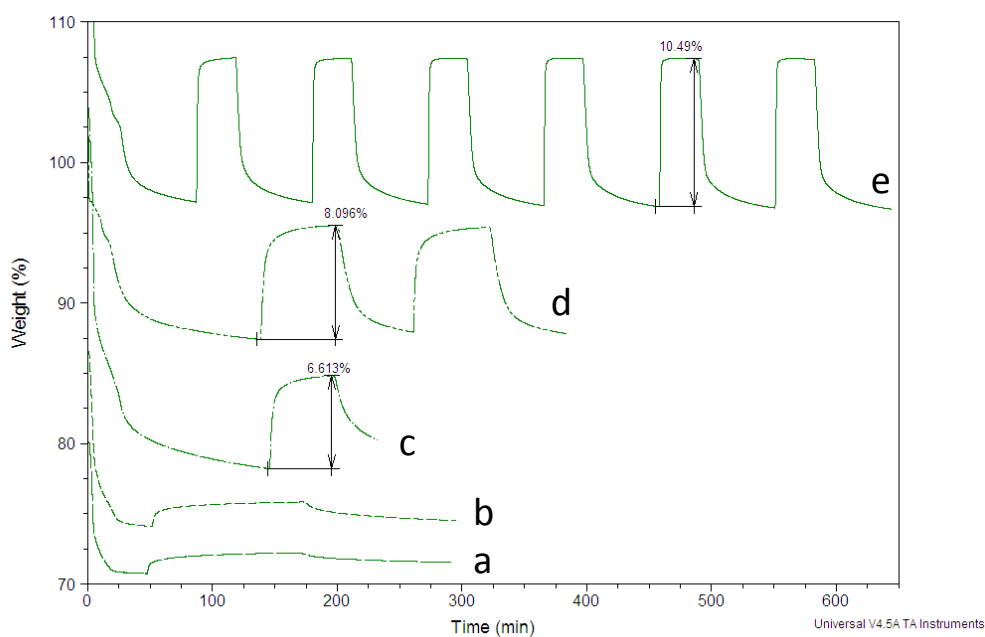
The effectiveness of the K-FA sorbents in capturing  $CO_2$  from a diluted stream was investigated. Figures 8 and 9 show the variation of the  $CO_2$  working capacity for the K-FA 2:1 and K-FA 1:1 in presence or absence of 10%  $Li_2CO_3$ . The  $CO_2$  uptake with diluted  $CO_2$  (14%) were lower than those obtained in presence of pure  $CO_2$  at 500°C, similar at 600°C and somehow higher at 700°C (1.08 mmol  $CO_2$  / g sorbent vs 0.82 for K-FA 2:1 and 1.50 vs 1.45 for K-FA 1:1) indicating that the eutectic melt favours  $CO_2$  diffusion in/out from the sorbent surface. However, the slopes of the sorption and desorption profiles suggest lower reaction rates compared with those in presence of pure  $CO_2$  stream and also, desorption was not completed in reasonable times. Diluted  $CO_2$  resulted in a lower  $CO_2$  sorption when the K-FA 1:1 was tested in presence of 10%  $Li_2CO_3$  (1.84 mmol  $CO_2$  / g sorbent vs 2.39), but reactions

occurred faster and desorption was completed, compared to the tests carried out in absence of additive.

A 500 MW coal-fired power plant with 90% CO<sub>2</sub> capture (~419,000 kg CO<sub>2</sub>/h) was considered to evaluate the potential industrial scale application of the developed sorbent.



**Figure 8.** K-FA 2:1 CO<sub>2</sub> sorption at a) 500°C, b) 600°C and c) 700°C in presence of 14%CO<sub>2</sub>.



**Figure 9.** CO<sub>2</sub> sorption of K-FA 1:1. a) 100%CO<sub>2</sub> at 500°C; b) 100%CO<sub>2</sub> at 600°C; c) 100%CO<sub>2</sub> at 700°C; d) 14%CO<sub>2</sub> at 700°C in presence of 10% Li<sub>2</sub>CO<sub>3</sub>; e) 100%CO<sub>2</sub> at 700°C in presence of 10% Li<sub>2</sub>CO<sub>3</sub>.

The capture plant was sized considering fix bed units able to load a total of 28000 kg of sorbent, as in previous work, to evaluate the feasibility of the developed sorbents (Quinn et al, 2012).

K-FA 1:1 - 10% Li<sub>2</sub>CO<sub>3</sub> was selected for the calculations due to its high total CO<sub>2</sub> capacity of 2.4 mmol CO<sub>2</sub>/g sorbent after 1 hour at 700°C, as can be seen in Table 3. Also, a flue gas containing 14%CO<sub>2</sub> (balanced with N<sub>2</sub>) was considered.

Four hypothetical cases were considered with adsorption taking place in 60, 30, 15 and 5 minutes to show how uptake time affects the hypothetical plant footprint. The number of reactors required to capture 90% of the CO<sub>2</sub> emitted in a 500 MW coal power plant is summarised in Table 3. Since the calculated number of vessels based on 60 minutes were very large (3.9 mmol CO<sub>2</sub>/g sorbent for a total of 140 vessels), they were not reported in the table. However, taking advantage of the rapid sorption and desorption rates of the K-FA sorbent in presence of the Li<sub>2</sub>CO<sub>3</sub> sorption promoter (10 wt%), the process became feasible at 5 minutes sorption time in presence of pure CO<sub>2</sub> stream, with only 12 vessels in parallel required for the CO<sub>2</sub> uptake, which would result in reduced capital costs. As expected, the CO<sub>2</sub> sorption capacity in presence of diluted CO<sub>2</sub> stream (14% CO<sub>2</sub> balanced with N<sub>2</sub>) is lower than in presence of pure CO<sub>2</sub> and this affects the foot-print of the hypothetical CO<sub>2</sub> capture plant, where 20 reactors would be required.

**Table 3.** CO<sub>2</sub> sorption capacity at different times and number of reactors required to capture 90% of CO<sub>2</sub> from a 500 MW coal-fired power plant with 90% CO<sub>2</sub> capture (~ 419,000 kg CO<sub>2</sub>/h). na: non available.

| CO <sub>2</sub> sorption, mmol CO <sub>2</sub> /g sorbent |      |      |      |      |
|---|------|------|------|------|
| Time, min   | 5    | 10   | 15   | 30   |
| K-FA 1:1  | 2.38 | 2.4  | 2.4  | 2.4  |
| K-FA 2:1  | 1.44 | 1.58 | 1.67 | 1.78 |
| Reactors required for CO <sub>2</sub> sorption            |      |      |      |      |
| K-FA 1:1 - 100%CO <sub>2</sub>                            | 12   | 24   | 35   | 71   |
| K-FA 1:1 - 14%CO <sub>2</sub>                             | 20   | 51   | na   | na   |

Amount of sorbents can be lowered by employing rapid thermal swing chemisorption (RTSC) process that utilizes shell and tube type vessels to minimize heating and cooling time (Lee and Sircar, 2008). Calculations indicated a 24% reduction in capital cost and a 78%



reduction in operating cost relative to conventional MEA technology may be achievable (Quinn et al, 2012). For example, the K-FA sorbent able to load 2.38 mmol CO<sub>2</sub>/g sorbent would result in 0.37 t to be loaded in the RTSC. Further works are required to evaluate the potential use of these sorbents with rapid sorption/desorption processes in presence of moisture.

## Conclusions

Potassium-fly ash (K-FA) CO<sub>2</sub> chemisorption at high temperature was evaluated using isothermal and cyclic thermo-gravimetric analyses in presence of 100% and 14% CO<sub>2</sub>. Lithium carbonate and calcium hydroxide were also evaluated as CO<sub>2</sub> sorption promoters. Temperature strongly affected the performance of the K-FA sorbents, resulting in a CO<sub>2</sub> uptake of 1.45 mmol CO<sub>2</sub>/g sorbent for K-FA 1:1 at 700°C. The CO<sub>2</sub> sorption was enhanced by the presence of lithium carbonate (10 wt%), with the K-FA 1:1 capturing 2.38 mmol CO<sub>2</sub>/g sorbent at 700°C in 5 minutes. The presence of 10% Li<sub>2</sub>CO<sub>3</sub> also accelerated sorption and desorption. The results suggest that the increased uptake of CO<sub>2</sub> and faster reaction rates in presence of K-FA can be ascribed to the formation of K-Li eutectic phase, which favours the diffusion of potassium and CO<sub>2</sub> in the material matrix. The cyclic experiments showed that the K-FA materials maintained stable CO<sub>2</sub> uptake and reaction rates over 10 cycles. Thanks to the rapid CO<sub>2</sub> sorption/desorption of the K-FA sorbent with Li<sub>2</sub>CO<sub>3</sub> (10 wt%), the process would require only 12 fix bed units for the sorption of 90% of the CO<sub>2</sub> emitted in a 500 MW coal power plant. As expected, the CO<sub>2</sub> sorption capacity in presence of 14% CO<sub>2</sub> affects the foot-print of the hypothetical CO<sub>2</sub> capture plant, where 20 reactors would be required.

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